

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-357901

(43)Date of publication of application : 13.12.2002

(51)Int.Cl. G03F 7/033
 C08F212/14
 C08F220/34
 C08F220/58
 G02B 5/20
 G03F 7/004
 G03F 7/11
 G03F 7/40

(21)Application number : 2001-164201

(71)Applicant : FUJI PHOTO FILM CO LTD

(22)Date of filing : 31.05.2001

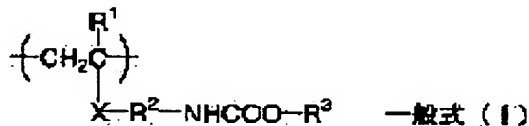
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(54) PHOTSENSITIVE RESIN COMPOSITION, TRANSFER MATERIAL AND IMAGE FORMING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a photosensitive resin composition or a transfer material being developable with a low alkaline developing solution even in the case of any of positive type and negative type photosensitive resin compositions or a photosensitive resin layer transfer material, having high resolution giving a pattern having excellent removing solution resistance after heat curing and exhibiting excellent aging stability of a photosensitive material.

SOLUTION: In the photosensitive resin composition which contains at least an alkali-soluble binder and a photosensitive component and is solubilized or insolubilized by irradiation with light, the alkali-soluble binder is a copolymer having at least a structural unit having a carboxyl group and a structural unit of formula (I).



LEGAL STATUS

[Date of request for examination]

10.01.2006

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

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CLAIMS

[Claim (a)]

[Claim 1] The photopolymer constituent with which this alkali fusibility binder is characterized by being the copolymer which has the structural unit which has a carboxyl group at least, and the structural unit expressed with the following general formula (I) in the photopolymer constituent which contains an alkali fusibility binder and a photosensitive component at least, and solubilizes or insolubilizes by optical exposure.

[Formula 1]



the inside of [type (I), and R¹ — a hydrogen atom or a methyl group — expressing — R² — the divalent hydrocarbon group (this hydrocarbon group — a straight chain —) of single bond or carbon numbers 1-10 branching or a ring structure — you may form — moreover — on the way — also — the ether and an ester bond — you may mind — the hydrocarbon group in which it may express and R³ may have the substituent of carbon numbers 1-18, and —N=C (R⁴) R⁵ (it is here) The hydrocarbon group in which R⁴ and R⁵ may have a hydrogen atom and the substituent of carbon numbers 1-18 (however, R⁴ and R⁵ not becoming a hydrogen atom at coincidence), and R⁴ and R⁵ — a ring — you may form — expressing, X expresses —CO—, —COO—, —OCO—, —CONH—, —NHCO—, and a phenylene group.]

[Claim 2] The negative-mold photopolymer constituent which is the combination of the compound with which this photosensitive component has two or more ethylene nature unsaturated bonds in claim 1, a photopolymerization initiator, or a photopolymerization initiator system.

[Claim 3] The positive type photopolymer constituent this whose photosensitive component is the photosensitive matter of 1 and 2-quinone diazide system in claim 1.

[Claim 4] the structural unit expressed with 5-50-mol % and a general formula (I) in either of claims 1-3 in the structural unit in which this alkali fusibility binder has a carboxyl group at least — 5 — 80-mol % — the photopolymer constituent which is the copolymer which it has.

[Claim 5] The photopolymer layer imprint ingredient characterized by preparing the layer which consists of a photopolymer constituent according to claim 1 to 4 on a temporary base material.

[Claim 6] The imprint ingredient which prepared the alkali fusibility thermoplastics layer, the interlayer, and the layer that consists of a photopolymer constituent according to claim 1 to 4 on the temporary base material at this order.

[Claim 7] The image formation approach characterized by carrying out pattern exposure, forming the pattern of a photopolymer layer on a base material by development, and heating the whole surface at 150 degrees C or more after exposure by ultraviolet rays further after preparing the constituent layer based on either of claims 1-6 on the base which has transparent conductive wiring.

[Claim 8] The image formation approach of carrying out pattern exposure, forming the pattern of a photopolymer layer on a base material by development, and heating the whole surface after

exposure by ultraviolet rays to it at 150 degrees C or more after preparing the constituent layer based on either of claims 1-7 in the base which has transparent conductive wiring on a color filter layer or in the bottom.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the suitable image formation approach to manufacture said structure about a photopolymer constituent, an imprint ingredient, and the image formation approach with the resin constituent for forming spacers for panels, such as a liquid crystal display component, the orientation division control material on an insulator layer and a color filter, the overcoat material for flattening, etc., the imprint ingredient which has this resin constituent layer, and a lamination method.

[0002]

[Description of the Prior Art] In recent years, the needs of the structure formation with detailed resolution of about 5 to about 20 microns of transparency and height of about 1 to about 10 microns are expanded. For example, they are the insulator layer for the micro condenser lens for color filters, the spacer for liquid crystal display panels, and high aperture method (it abbreviates to HA method below) liquid crystal displays, the insulator layer for color filter-on array method (it abbreviates to COA method below) liquid crystal displays, the structure for orientation division on a color filter, a liquid crystal orientation control material for plasma address system liquid crystal displays, the overcoat material for flattening on a color filter, etc.

[0003] What consists of a component of a photosensitive component, a cross linking agent, resin, or cross-linking resin has been conventionally used at these purposes like the resin constituent which added the epoxy cross linking agent to the positive type photosensitivity matter, and the resin constituent which added the epoxy cross linking agent to the negative-mold photosensitivity matter.

[0004] For example, the JP.3-223702.A specification is asked for alkali fusibility resin and the positive type sensitive material for lens formation which consists of 1, 2-naphthoquinonediazide sulfonate, a heat-curing agent, and a solvent as a sensitization agent. As a cross linking agent, the ARUKI roll melamine system cross linking agent is mentioned. There is a publication that pattern formation is carried out with photolithography after forming a paint film and a micro condenser lens can be formed at 100 to 160 degrees C on a color filter using this ingredient by the thing for about 1 to 30 minutes to do for time amount on heat-treatment.

[0005] Moreover, JP.5-158232.A is asked for the copolymer of hydroxystyrene and methyl methacrylate, the quinone diazide radical content compound, and the positive type photoresist constituent containing thermosetting resin, an optical exposure and development perform heat-treatment for 2 to 15 minutes at 100 to 300 degrees C after pattern formation and an ultraviolet-rays complete exposure, and the approach of fluidizing a pattern and forming a semicircle ball-like micro lens is indicated. As thermosetting resin, melamine resin, a urea-resin, alkyl methyl methacrylate melamine resin, and an alkoxy methylation urea-resin are mentioned.

[0006] Moreover, JP.5-2947350 has a technical indication that the angle of visibility in a liquid crystal display is improved, as a result of realizing orientation division, if the projection pattern of zigzag is formed on a liquid crystal cell substrate and the liquid crystal orientation film is formed on it. The novolak mold photoresist is used as a projection pattern formation ingredient. Moreover, it is indicated that the orientation where the cross section of a projection pattern was

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the curing agent probably contained in this constituent is unstable in a system.

[0013] Then, the example using the block isocyanate system compound which is the precursor of an isocyanate radical as a new curing agent for solving these problems is known, as such an example — JP.3-50549.A — said — 7-278254 — said — 8-15861 — said — the constituent containing the compound which blocked the binder resin and the polyfunctional monomer which have the carboxyl group of 10-20505 and this 10-148938 grade, a photopolymerization initiator, and the poly isocyanate of two or more organic functions is indicated. Although surely it passed through these curing agents as compared with the conventional curing agent and the Tokiyasu quality was improved sharply, the hardenability was falling conversely and the resistance to processing liquid, such as exfoliation liquid resistance, etc. was not what can still be satisfied fully.

[0014] Thus, in the photopolymer constituent for forming spacers for panels, such as a liquid crystal display component, the orientation division control material on an insulator layer and a color filter, the overcoat material for flattening, etc., and the imprint ingredient which has this resin constituent layer, a constituent and an imprint ingredient which are satisfied with coincidence of various processing liquid resistance, such as exfoliation liquid, and the stability with the passage of time as sensitization material regardless of a negative mold and a positive type with the development nature which is a basic property are not known.

[0015]

[Problem(s) to be Solved by the Invention] This invention was devised [making the engine-performance improvement of the conventional ingredient, and] by the 1st purpose in view of these situations. That is, since the preservation stability of a photopolymer constituent is excellent, it is easy to use it, and development is possible in a with a pH of about ten weak alkaline water solution, resolution is high, and it aims at offering the photopolymer constituent which is excellent also in thermal resistance and various kinds of processing liquid resistance after heat curing, especially a photosensitive thermosetting resin constituent. A photosensitive layer can be formed on a substrate by carrying out spreading desiccation of the constituent of this invention by the usual approach on a substrate as photosensitive coating liquid. Moreover, it is in the 2nd purpose of this invention offering the photopolymer layer imprint ingredient excellent in the preservation stability which can manufacture the coating article which was rich in usable flexibility with the replica method, and can give the image excellent in development nature, definition, thermal resistance, and various kinds of processing liquid resistance, especially a photosensitive thermosetting resin layer imprint ingredient. Furthermore, the 3rd purpose of this invention is to offer the suitable image formation approach to manufacture spacers for panels, such as a liquid crystal display component, the orientation division control material on an insulator layer and a color filter, the overcoat material for flattening, etc.

[0016]

[Means for Solving the Problem] this invention person etc. came to complete a header and this invention for these problems being solvable by using the following, as a result of inquiring wholeheartedly, in order to solve these technical problems. That is, the means of the invention in this application is as follows.

[0017] <1> Photopolymer constituent with which this alkali fusibility binder is characterized by being the copolymer which has the structural unit which has a carboxyl group at least, and the structural unit expressed with the following general formula (I) in the photopolymer constituent which contains an alkali fusibility binder and a photosensitive component at least, and solubilizes or insolubilizes by optical exposure.

[Formula 2]



the inside of [type (I), and R¹ — a hydrogen atom or a methyl group — expressing — R² — the divalent hydrocarbon group (this hydrocarbon group — a straight chain —) of single bond or

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stabilized more by the projection pattern of a boiled-fish-paste (cyfnder) form is obtained.

However, as a projection pattern formation ingredient, when a novolak mold photoresist was used, there was a problem that slight coloring and thermal resistance, and chemical resistance were insufficient in the boiled-fish-paste-like projection pattern after BEKU. Although the micro lens excellent in a configuration and transparency and the projection pattern could be formed with these constituents, when cross linking agents, such as melamine resin, were not included, the problem was in thermal resistance and solvent resistance, and since the preservation stability of a photosensitive constituent was inadequate when a well-known cross linking agent is included, there was fault on the occasion of practical use.

[0007] In order to realize the liquid crystal display of HA method, the approach of forming the structure of insulating transparency resin on a TFT array substrate is proposed by U.S. Pat. No. 5641974. As the example, for connection between a transparent electrode and a drain, in order to perform contact hole formation, use of about five or less benz-cyclo-butene (BCB) of a dielectric constant or a transparent photopolymerization system photopolymer is indicated as a photopolymer of a negative mold. The liquid crystal display of the COA method which realizes a high numerical aperture is indicated by forming an insulating color filter in a TFT substrate side by U.S. Pat. No. 5994721. Moreover, how to form a transparent and colorless insulating photopolymer layer on a color filter layer is also indicated. The object for spacers for liquid crystal displays or the radiation-curing nature constituent for protective layers containing an acrylic copolymer, an acidic group content monomer / allyl compound methacrylate copolymer, a radiation-sensitive compound, and a solvent is indicated by JP.11-323057.A.

[0008] Although these negative-mold photopolymers were excellent in transparency and insulation, the resistance (chemical resistance) over the organic solvent system exfoliation liquid used at the exfoliation process of etching resist was inadequate. The constituent which consists of a polymer acid binder, polyfunctional monomer, a photoinitiator, and an aldehyde condensation resin precursor is proposed by JP.59-151152.A. Although the hardening film obtained from this constituent is excellent also in transparency and chemical resistance, it is insufficient of the preservation stability of a constituent too.

[0009] The method of carrying out spreading desiccation of the photosensitive constituent on a film base material beforehand, providing as a film resist on the other hand, imprinting a photosensitive layer on a substrate using it, and giving a photosensitive layer on a substrate is called a replica method, and thin film formation for the sex from Takao and high quality is possible for it. The approach which used this type of ingredient is indicated by JP.10-97061.A and JP.10-206888.A. That is, an overcoat film (negative mold) is stuck by the laminating method, and the approach of forming the interlayer insulation film which has the description in performing pattern NINGU is indicated.

[0010] Although it was the replica method which has such a description, there was no still practical thing at the photoresist of the conventional positive type. Since that to which an old positive type uses 1 and 2-naphthoquinonediazide sulfonate as a photosensitive component by using phenol novolak resin as a principal component was most, its membranous quality is weak, and since this cause lacks in flexibility, it is because the difficulty was to consider as a roll-like product as a film-like paint film.

[0011] That is, although usually carrying out a slit from a large roll is performed in order to process it into the roll product of the decided width of face, in the coating article of weak membranous quality, scraps will be generated in the case of this slit. Moreover, although hot printing was carried out usually sticking the roll-like photoresist as a coating article on a film to the substrate which should be processed with photolithography by pressure with a laminator, it was difficult to pollute the operation environment of a substrate or a laminator with the process out into the size of the longitudinal direction of a substrate also in this case for scraps generating, and to obtain as few imprint layers of a defect.

[0012] Although the film plasticity was good when this constituent was used on the other hand, although the constituent which used alkali fusibility acrylic resin was proposed by above-mentioned JP.3-223702.A, the preservation stability in a film condition, the solvent resistance of the image after hardening, and thermal resistance were still inadequate. It is considered because

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carbon numbers 1-10 branching or a ring structure — you may form — moreover — on the way — alkene — the ether and an ester bond — you may mind — the hydrocarbon group in which it may express and R³ may have the substituent of carbon numbers 1-18, and —N=C(R⁴)R⁵ (it is here) The hydrocarbon group in which R⁴ and R⁵ may have a hydrogen atom and the substituent of carbon numbers 1-18 (however, R⁴ and R⁵ not becoming a hydrogen atom at coincidence), and R⁴ and R⁵ — a ring — you may form — expressing X expresses —CO—, —COO—, —OCO—, —CONH—, —NHCO—, and a phenylene group.]

<2> Negative-mold photopolymer constituent which is the combination of the compound with which this photosensitive component has two or more ethylene nature unsaturated bonds in the above <1>, a photopolymerization initiator, or a photopolymerization initiator system.

<3> Positive type photopolymer constituent this whose photosensitive component is the photosensitive matter of 1 and 2-quinone diazide system in the above <1>.

<4> the structural unit expressed with 5-50-mol % and a general formula (I) in either of above-mentioned <1>—<3> in the structural unit in which this alkali fusibility binder has a carboxyl group at least — 5-80-mol % — photopolymer constituent which is the copolymer which it has.

<5> Photopolymer layer imprint ingredient characterized by preparing the layer which becomes either of above-mentioned <1>—<4> from the photopolymer constituent of a publication on a temporary base material.

<6> Imprint ingredient which prepared the layer which becomes either of <1>—<3> an alkali fusibility thermoplastics layer, an interlayer, and above-mentioned from the photopolymer constituent of a publication on the temporary base material at this order.

<7> The image formation approach characterized by carrying out pattern exposure, forming the pattern of a photopolymer layer on a base material by development, and heating the whole surface at 150 degrees C or more after exposure by ultraviolet rays further after preparing the constituent layer based on either of above-mentioned <1>—<6> on the base which has transparent conductive wiring.

<8> The image formation approach of carrying out pattern exposure, forming the pattern of a photopolymer layer on a base material by development, and heating the whole surface after exposure by ultraviolet rays to it at 150 degrees C or more after preparing the constituent layer based on either of above-mentioned <1>—<7> in the base which has transparent conductive wiring on a color filter layer or in the bottom.

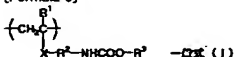
[0018]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[Copolymer of this invention] The photopolymer constituent of this invention is characterized by being the photopolymer constituent which contains an alkali fusibility binder and a photosensitive component at least, and solubilizes or insolubilizes by optical exposure, and this alkali fusibility binder being the copolymer which has the structural unit which has a carboxyl group at least, and the structural unit expressed with the following general formula (I) as an indispensable component.

[0019]

[Formula 3]



[0020] the inside of an upper type (I), and R¹ — a hydrogen atom or a methyl group — expressing — R² — the divalent hydrocarbon group (this hydrocarbon group — a straight chain —) of single bond or carbon numbers 1-10 branching or a ring structure — you may form — moreover — on the way — alkene — the ether and an ester bond — you may mind — the hydrocarbon group in which it may express and R³ may have the substituent of carbon numbers 1-18, and —N=C(R⁴)R⁵ (it is here) The hydrocarbon group in which R⁴ and R⁵ may have a hydrogen atom and the substituent of carbon numbers 1-18 (however, R⁴ and R⁵ not become

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a hydrogen atom at) coincidence — expressing — R4 and R5 — a ring — you may form — expressing, X expresses —CO—, —COO—, —OCO—, —CONH—, —NHCO—, and a phenylene group. [Moreover,]

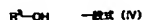
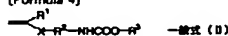
[0021] As R2 in a general formula (I), alkynes, such as single bond and n(CH2)1 (n1 is the integer of 1 to 10), Annular alkynes, such as branching alkynes, such as isopropylidene, and cyclo hexylene. The radical which has aromatic series rings, such as phenylene, tokylene, xylylene, and naphthylene, (C2H4O)2 the thing (m1 — the integer of 1 to 5 —) through ether linkage, such as m1 and m (C3H6O)2 That m2 minds ester bonds, such as the integer of 1 to 3, p (CH2)1-OCO-(CH2) p2, and p(CH2)1-COO-(CH2) p2, (p1+p2 are the integer of 1-9). Furthermore, such combination etc. is mentioned to the thing and list through the double bond between carbon, and a triple bond.

[0022] as R3 in a general formula (I) — alkyl (for example, methyl and ethyl —) n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, hexyl, 2-ethylhexyl, DESHURU, dodecyl, octadecyl. Radicals, such as an alkyl compound, annular alkyl radicals (for example, cyclopentyl, cyclohexyl, etc.). Atrial radicals (for example, benzyl, phenethyl, etc.), aryl radicals (for example, phenyl, naphthyl, etc.), and the things (TORIFURORO ethyl, hexa FURORO isopropyl, methoxyphenyl, etc.) that contain a substituent further are mentioned. Moreover, the above R3 may be shown by —N=C (R4) R5. R4 and R5 may carry out a hydrogen atom or the same radical (however, R4 and R5 do not become a hydrogen atom at coincidence) as said R3 here, and a ring may be formed by R4 and R5 (for example, cyclohexylidene etc.).

[0023] The above-mentioned copolymer of this invention is obtained by carrying out copolymerization of the monomer of copolymerizable others to these by the well-known approach the polymerization nature monomer shown by the polymerization nature monomer which has a carboxyl group, and the following general formula (III), and if needed. Or after copolymerizing these and a copolymerizable monomer the isocyanate radical content monomer shown by the polymerization nature monomer which has a carboxyl group, and the following general formula (III), and if needed, it is obtained also by the macromolecule reaction with the hydroxyl group-containing compound shown by the following general formula (IV). However, since the addition reaction of a carboxyl group and the isocyanate radical in the compound of the following general formula (III) may advance during a copolymerization reaction, the former synthetic approach is desirable.

[0024]

[Formula 4]



R1, R2, R3, and X in an upper type are synonymous with R1, R2, R3, and X in said general formula (I) respectively.

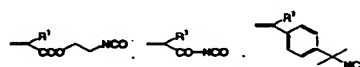
[0025] The monomer shown by the general formula (III) is obtained by the addition reaction of the compound shown by the isocyanate radical content monomer shown by the general formula (III), and the general formula (IV). This addition reaction is under a room temperature or a heating condition in aprotic solvents (for example, an acetonitrile, a tetrahydrofuran, ethyl acetate, chloroform, etc.), or is obtained by heating a room temperature or if needed under coexistence of a catalyst, such as a tin system compound and tertiary amine, etc.

[0026] As an example of an isocyanate radical content monomer shown by said general formula (III), the following compounds are mentioned, for example.

[Formula 5]

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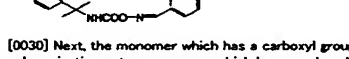
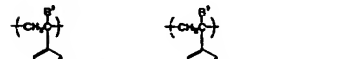
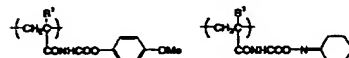
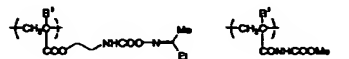
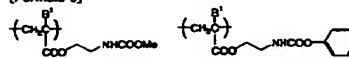


[0027] As hydroxyl group-containing compound expressed with said general formula (IV) alcohols (a methanol, ethanol, n-propanol, and i-propanol —) n-butanol, i-butanol, a sec-butanol, t-butanol, n-hexanol, a cyclohexanol, n-hexanol, 2-ethylhexanol, n-decanol, n dodecanol, OKUTA decanol, benzyl alcohol, Phenols, such as phenyl ethyl alcohol and vinylbenzyl alcohol, and oximes (a phenol, cresol, naphthyl alcohol, etc.) (a methyl ketone oxime, cyclohexanone oxime, etc.) are mentioned.

[0028] Furthermore, as what has a substituent, FURORO ethanol, triphloro ethanol, methoxy ethanol, phenoxymethanol, chlorophenol, dichlorophenol, a methoxy phenol, an acetoxyl phenol, etc. are mentioned. One sort or two or more sorts of combination are sufficient as these compounds.

[0029] Furthermore, as a concrete example of the compound which has the structural unit expressed with said general formula (II), the following is mentioned, for example. R1 in a bottom type shows a hydrogen atom or a methyl group.

[Formula 6]



[0030] Next, the monomer which has a carboxyl group is explained to a detail. As a polymerization nature monomer which has a carboxyl group, an acrylic acid, a vinyl benzoic acid, a maleic acid, an itaconic acid, a crotonic acid, cinnamic acid, an acrylic-acid dimer, etc. are

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mentioned, for example (meta). Moreover, the addition reaction object of the monomer and a cyclic anhydride like a maleic anhydride or phthalic anhydride which have hydroxyl groups, such as 2-hydroxyethyl (meta) acrylate, can also be used. Moreover, an anhydride monomer like a maleic anhydride and itaconic acid anhydride can also be used as a precursor of a carboxylic acid. Especially in these, the point (meta) of polymerization nature or raw material cost to an acrylic acid is desirable. One sort or two or more sorts of combination are sufficient as the polymerization nature monomer which has these carboxyl groups.

[0031] moreover, as a monomer of others in which these structural units and copolymerization are possible For example, acrylic-acid (meta) alkyl ester [(meta), for example, a methyl acrylate, An ethyl acrylate, acrylic-acid (meta) propyl, acrylic-acid (meta) isopropyl, (Meta) Acrylic-acid n-butyl, isobutyl acrylate (meta), acrylic-acid (meta) t-butyl, (Meta) Acrylic-acid hexyl, acrylic-acid (meta) octyl, 2-ethylhexyl acrylate (meta), (Meta)], such as acrylic-acid (meta) C1-18 alkyl ester, such as acrylic-acid lauryl and acrylic-acid (meta) stearyl, (Meta) Acrylic-acid cycloalkyl ester [(meta) acrylic-acid cyclohexyl] etc., (Meta) (Meta) acrylic-acid aryl ester [(meta) acrylic-acid phenyl etc. aralkyls] ester [(meta) acrylic-acid benzyl etc. perfluorinated] (meta) acrylic-acid alkyl ester [— for example Acrylic-acid 2-hydroxyethyl, dimethylaminoethyl (meta) acrylate, (Meta)], such as diethylaminoethyl (meta) acrylate, dimethylaminopropyl (meta) acrylate, and diethylamino propyl (meta) acrylate, and AKURI (meta) amides [— for example (Meta)] and perfluorinated (meta) AKURI amides [— such as acrylamide, dimethyl (meta) acrylamide, isopropyl (meta) acrylamide and t-butyl (meta) acrylamide] [— for example], such as acryloyl morpholine and dimethylaminopropyl (meta) acrylamide, (Meta) Aromatic series vinyl [styrene, vinyltoluene, alpha methyl styrene], etc. Heterocycle vinyl [vinyl imidazole, vinylpyridine, etc. vinyl ester] [vinyl acetate,] and N-vinyl amides [— such as propionic acid vinyl and BASA tic acid vinyl,] [N-vinyl pyrrolidone,] such as N-vinyl formamide and N-vinyl acetamide, and allyl ester [an acetic-acid alkyl compound] etc. A halogen content monomer [a vinylidene chloride, a vinyl chloride], etc., vinylcyanide [(meta) acrylonitrile] etc., and olefins [ethylene, a propylene], etc. are mentioned.

[0032] among these — also coming out — acrylic-acid alkyl ester [— from copolymeric / the /, the solvent solubility (meta) of the polymer to generate, etc.] [— for example A methyl acrylate, an ethyl acrylate (meta), acrylic-acid (meta) propyl, (Meta) Acrylic-acid isopropyl, acrylic-acid (meta) n-butyl, (Meta) Isobutyl acrylate, acrylic-acid (meta) t-butyl, acrylic-acid (meta) hexyl, (Meta) (Meta)] and acrylic-acid (meta) cycloalkyl ester [(meta) acrylic-acid cyclohexyl] etc., such as acrylic-acid octyl and 2-ethylhexyl acrylate (meta), especially aralkyl ester [(meta) acrylic-acid benzyl] etc., etc. are desirable. One sort or two or more sorts of combination are sufficient as these copolymerizable components.

[0033] the structural unit expressed with 5-50-mol % and said general formula (I) in the structural unit in which the structural unit presentation ratio of the copolymer mentioned above has a carboxyl group at least in the photopolymer constituent of this invention — 5 — 80-mol % — it is desirable that it is the copolymer which it has, 5 — 60-mol % has the still more desirable structural unit shown by the general formula (I), and especially 10 — 50-mol % is desirable. If exfoliation liquid resistance may be less than [5 mol %] insufficient for the structural unit shown by this general formula (I) and it exceeds 80-mol %, development nature may fall. Moreover, 10-40-mol % is still more desirable in the structural unit which has a carboxyl group, and especially 15-40-mol % is desirable. If development nature may be less than [5 mol %] insufficient for the structural unit which has a carboxyl group and it exceeds 50-mol %, exfoliation liquid resistance may fall.

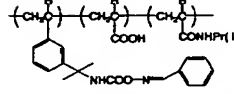
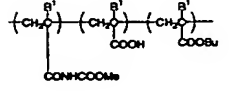
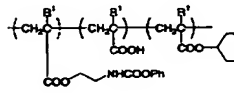
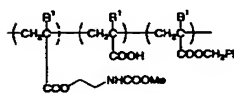
[0034] moreover, the mass average molecular weight of these copolymers — 5000-200,000 — desirable — 10,000-100,000 — further — desirable — 15,000- especially 80,000 is desirable. When manufacture of a copolymer may be difficult for mass average molecular weight at less than 5000 and it exceeds 200,000, development nature may fall.

[0035] As an example of the copolymer of this invention mentioned above, the following is mentioned, for example.

[Formula 7]

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[0036] Such a copolymer is obtained by carrying out copolymerization of the monomer which carries out considerable, respectively according to a conventional method by the well-known approach. For example, it is obtained by dissolving these monomers into a suitable solvent, adding a radical polymerization initiator there, and carrying out a polymerization in a solution. Or where these monomers are distributed in an aqueous medium, the so-called emulsion polymerization may perform a polymerization.

[0037] Although it can be chosen as arbitration as an example of a suitable solvent according to the solubility of the monomer to be used and the copolymer to generate, a methanol, ethanol, propanol, isopropanol, 1-methoxy-2-propanol, an acetone, a methyl ethyl ketone, methyl isobutyl ketone, methoxy propyl acetate, ethyl lactate, ethyl acetate, an acetonitrile, a tetrahydrofuran, dimethylformamide, chloroform, toluene, such mixture, etc. can be used, for example. Moreover, an azo system like 2 and 2'-azobis (isobutyronitrile) (azobisisobutyronitrile), 2, 2'-azobis - (2, 4'-dimethylvaleronitrile) as a polymerization initiator, a peroxide system like benzoyl peroxide, persulfate, etc. can be used.

[0038] (Photosensitive component) Next, a photosensitive component is explained to a detail. In the photopolymer constituent of this invention, various kinds of well-known photosensitive components can be used. The photosensitive matter of 1 and 2-quinone diazide system which acts on the combination of the compound, photopolymerization initiator, or photopolymerization initiator system which more specifically has two or more ethylene nature unsaturated bonds which act on a negative mold, and a positive type is mentioned as a suitable example.

[0039] It is desirable to contain the combination of the compound in which addition polymerization is possible, photopolymerization initiator, or photopolymerization initiator system which has two or more ethylene nature unsaturated bonds as a negative-mold photopolymer of

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4-sulfonate, 2, 4, 6, 3', 4', and 5 - ' - hexa hydroxy benzophenone -1 and a 2-naphthoquinonediazide-5-sulfonate - 3, 4, 5, 3', 4', and 5 - ' - hexa hydroxy benzophenone -1 and a 2-naphthoquinonediazide-4-sulfonate - 3, 4, 5, 3', 4', and 5 - ' - 1 of hexa hydroxy benzophenone, such as - hexa hydroxy benzophenone -1 and a 2-naphthoquinonediazide-5-sulfonate, and 2-naphthoquinonediazide sulfonate;

[0068] Bis(2, 4-dihydroxy phenyl) methane -1, a 2-naphthoquinonediazide-4-sulfonate, Bis(2, 4-dihydroxy phenyl) methane -1, a 2-naphthoquinonediazide-5-sulfonate, Bis(p-hydroxyphenyl) methane -1, a 2-naphthoquinonediazide-4-sulfonate, Bis(p-hydroxyphenyl) methane -1, a 2-naphthoquinonediazide-5-sulfonate, Tori (p-hydroxyphenyl) methane -1, a 2-naphthoquinonediazide-4-sulfonate, Tori (p-hydroxyphenyl) methane -1, a 2-naphthoquinonediazide-5-sulfonate, 1, 1, and 1-Tori (p-hydroxyphenyl) ethane -1, a 2-naphthoquinonediazide-4-sulfonate, 1, 1, and 1-Tori (p-hydroxyphenyl) ethane -1, a 2-naphthoquinonediazide-5-sulfonate, Bis(2, 3, 4-trihydroxy phenyl) methane -1, a 2-naphthoquinonediazide-4-sulfonate, Bis(2, 3, 4-trihydroxy phenyl) methane -1, a 2-naphthoquinonediazide-5-sulfonate, The 2 and 2-bis(2, 3, 4-trihydroxy phenyl) propane -1, a 2-naphthoquinonediazide-4-sulfonate, The 2 and 2-bis(2, 3, 4-trihydroxy phenyl) propane -1, a 2-naphthoquinonediazide-5-sulfonate, 1, 1, the 3-tris (2, 5-dimethyl-4-hydroxyphenyl)-3-phenyl propane -1, a 2-naphthoquinonediazide-4-sulfonate, 1, 1, the 3-tris (2, 5-dimethyl-4-hydroxyphenyl)-3-phenyl propane -1, a 2-naphthoquinonediazide-5-sulfonate, The 4 and 4'-[1-(4-[1-(4-hydroxyphenyl)-1-methylethyl] phenyl) ethyldiene] bisphenol -1, a 2-naphthoquinonediazide-4-sulfonate, The 4 and 4'-[1-(4-[1-(4-hydroxyphenyl)-1-methylethyl] phenyl) ethyldiene] bisphenol -1, a 2-naphthoquinonediazide-5-sulfonate, The bis(2, 5-dimethyl-4-hydroxyphenyl)-2-hydroxy phenylmethane -1, a 2-naphthoquinonediazide-4-sulfonate, The bis (2, 5-dimethyl-4-hydroxyphenyl)-2-hydroxy phenylmethane -1, a 2-naphthoquinonediazide-5-sulfonate, 3, 3, 3', 3'-tetramethyl - The 1 and 1' - Spirobi indene -5, 6 and 7, 5', 6', 7'-hexanol -1, a 2-naphthoquinonediazide-4-sulfonate, 3, 3, 3', 3'-tetramethyl - The 1 and 1' - Spirobi indene -5, 6 and 7, 5', 6', 7'-hexanol -1, a 2-naphthoquinonediazide-5-sulfonate, 2, 2, 4-trimethyl -7, 2', the 4'-trihydroxy flavan -1, a 2-naphthoquinonediazide-4-sulfonate, 2, 2, 4-trimethyl -1 of alkanes (polyhydroxy phenyl), such as 7, 2', the 4'-trihydroxy flavan -1, and a 2-naphthoquinonediazide-5-sulfonate, 2-naphthoquinonediazide sulfonate, etc. are mentioned. These 1 and 2-quinone diazide system compound are independent, or can use two or more kinds together, and can be used.

[0067] The desirable amount of these 1 and 2-quinone diazide system compound used is the 10 - 120 mass section, especially 20 - 80 mass section of the 100 mass sections of said copolymer. Since there are few amounts of the acid generated by the exposure of light when this rate is under 10 mass sections, the difference of the solubility to the alkali water solution used as the developer of an optical exposure part and a non-irradiated part may be small, and accurate patterning may become difficult. On the other hand, by short-time optical exposure, when this rate exceeds the 120 mass sections, since unreacted 1 and 2-quinone diazide system compound remain so much, the dissolution in said alkali water solution may be insufficient, and it may become difficult to develop negatives.

[0068] (Other components) In the photopolymer constituent of this invention, various kinds of additives can be added for the various purpose. As an example of an additive, they are a surfactant, an adhesion accelerator, a plasticizer, a decolorization nature coloring agent, etc.

[0069] As the above-mentioned surfactant, it can be used in order to raise spreading nature and the smooth nature of the paint film obtained. As the example for example, BM-1000 (product made from BM Chemie), megger facsimile F142D, said - F172 - said - F173 - said - F183 (above, Dainippon Ink & Chemicals, Inc. make) - Fluorad FC-135, this FC-170C, and Fluorad FC-430 - said - FC-431 (above) the Sumitomo 3M make and Sir chlorofluorcarbon S-112 - said - S-113 - said - S-131 - said - S-141 - said - S-145 (above) The fluorine system or silicone system surfactant marketed by the trade name of the Asahi Glass Co., Ltd. make, SH-28PA, SH-190, SH-193, SZ-6032, SF-8428, DC-57, and DC-190 (above, product made from Toray Industries Silicone) can be used. As for especially the amount of the surfactant used, it is desirable that they are below 2 mass sections below 5 mass sections to the total-solids 100

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negative mold, an unexposed part is removed in development using what NEGAPOUI of a mask reversed.)

Then, as shown in E process, UV exposure of the whole surface is carried out, the melt flow after exposure is made to start, and the cross-section configuration of contact hole 13B is made into a smooth tilt angle. [the temperature of 150 degrees C or more] [for 10 - 150 minutes] A hardening reaction occurs into this heat treatment process, and the photosensitive photoresist layer this exposed and developed is hardened. Entire UV light doses are usually 100 mJ/cm² - 1000 mJ/cm² depending on the content of 1 and 2-quinone diazide compound that it should just be a complement at the photolysis of 1 and 2-quinone diazide compound in the case of a positive type. In order to promote bridge formation by the polymerization further also in the case of a negative mold, it is desirable to include this exposure process. Then, as shown in F process, the ITO film 15 is usually formed by the sputter under the temperature of 180-250 degrees C. The thickness of ITO is usually 1500-2500Å (0.15-0.25 micrometers).

[0076] Then, as shown in G process, for a pattern chemically-modified [of upper ITO] degree, a coat is carried out to the whole surface, it dries, and UV light exposure of the photoresist 16 for ITO etching is carried out through the pattern mask 14 of upper ITO. The thickness after spreading desiccation of a photoresist is about 1 micrometer - about 3 micrometers. As shown in H process, ITO of the part which is not covered by the resist is dissolved by acid etching reagents, such as ferric chloride / usual hydrochloric-acid mixed liquor, a usual hydrobromic-acid water solution, etc., after the development of a resist image. A photoresist is removed by resist exfoliation liquid as shown in I process after that. Resist exfoliation liquid is indicated by JP.51-72503A, JP.57-84456A, U.S. Pat. No. 4165294, Europe public presentation JP.0119337B, JP.6-222573A, etc. As typical exfoliation liquid, the mixed liquor of 7:3 (mass ratio) of monoethanolamine and dimethyl sulfoxide is mentioned. An exfoliation process is performed by usually being immersed into this exfoliation liquid for [2 minutes -] 10 minutes at 50 degrees C - 80 degrees C. The photosensitive thermosetting layer by which heat curing was exposed and carried out at this time needs to show sufficient resistance to this exfoliation liquid. Otherwise, it is because ITO on an insulating layer ****s inconvenient. Moreover, an insulating layer needs to secure desired insulation. In order to realize insulation sufficient with a thin film, the dielectric constant of an insulating layer needs to be 3.5 or less preferably four or less.

[0077] As mentioned above, if the business of this COA or photosensitive thermosetting resin ***** in HA application is 1 liquefied constituent and it is spreading nature and a solid-state-like constituent, the laminating nature to a substrate, 2 image-formation nature (photograph nature), the heat flow nature after 3 image formation, the hardness after 4 heat flow (thermal resistance), exfoliation-proof [5] acidity or alkalinity, 6 insulation, its 7 transparent and colorless nature, etc. are main.

[0078] (Preparation of a photopolymer constituent) The photopolymer constituent of this invention can be prepared by mixing to homogeneity the component of others which are contained if needed including an aforementioned alkali fusibility binder and an aforementioned photosensitive component, dissolves each component in an organic solvent, and usually prepares it as a constituent solution. If the component of others which are contained as an organic solvent in here an alkali meltable binder, a photosensitive component, and if needed is dissolved and it does not react with these components, it is good anything.

[0079] As an example of such an organic solvent, ether; ethylene glycol monomethyl ether [such as an alcohols; tetrahydrofuran], such as a methanol and ethanol, Ethylene glycol wood ether, the ethylene glycol methylethyl ether, Glycol ether, such as ethylene glycol monoethyl ether; Methylcellosolve acetate, Ethylene glycol alkyl ether acetate, such as ethylcellosolve acetate; The diethylene glycol monomethyl ether, Diethylene glycol diethylether, diethylene glycol wood ether, Diethylene glycol ethyl methyl ether, diethylene glycol monoethyl ether, Diethylene glycols, such as the diethylene glycol monobutyl ether; Propylene glycol methyl ether acetate, Propylene glycol alkyl ether acetate, such as propylene glycol ethyl ether acetate; Toluene, Aromatic hydrocarbon, such as a xylene; A methyl ethyl ketone, a cyclohexanone, Ketones, such as 4-hydroxy-4-methyl-2-pentanone; 2-hydroxy ethyl propionate, 2-hydroxy-2-methyl methyl propionate, 2-hydroxy-2-methyl ethyl propionate, Ethoxy ethyl acetate,

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mass section.

[0070] Furthermore, in order to raise adhesion with a base, an adhesion accelerator can be made to contain as an additive in the photopolymer constituent of this invention. As such an adhesion accelerator, a functionality silane coupling agent can be used suitably. Here, a functionality silane coupling agent means the silane compound which has reactant substituents, such as a carbosyl group, a methacryloyl radical, an isocyanate radical, and an epoxy group, here, and a trimethoxysilyl benzoic acid, gamma-methacryloxypropyl trimethoxy silane, vinyltriethoxysilane, vinyltrimethoxysilane, gamma-isocyanate propyl triethoxysilane, gamma-glycidyloxypropyltrimethoxysilane, beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, etc. are mentioned as the example. As for especially the desirable amount of the adhesion accelerator used, it is desirable that it is 0.05 - 5 mass section below 10 mass sections to the total-solids 100 mass section.

[0071] Although it is desirable to be colored for the description of the photosensitive layer front face after spreading and inspection of a spreading defect at the time of use as for a photosensitive layer, a final hardening image needs a substantially transparent and colorless thing. It is desirable to contain the coloring agent decolorized by heating or optical exposure for this purpose.

[0072] As a decolorization nature coloring agent, what itself decomposes by the reaction with what is usually decolorized by decomposition at the temperature of 150 degrees C or more in process of heat treatment for [for / 10 minutes / -] 150 minutes, the thing which disperses out of a system, and other components, and is decolorized can be used. As those decolorization nature coloring agents, transparency is high in UV field, and the triphenylmethane dye which was excellent in decolorant after heat treatment can use it advantageously. For example, as a desirable color, a crystal violet, Methyl Violet, ethyl violet, oil blue #603, Victoria PYUA blue BOH, Malachite Green, diamond Green, etc. are mentioned, in addition the coloring agent of a publication can use it for JP.10-97061A, JP.10-104827A, or JP.3-68375B advantageously. The desirable amount of the decolorization nature coloring agent used is below 10 mass sections to the total-solids 100 mass section, and its 0.05 - 5 mass section is especially desirable.

[0073] (Application of a photopolymer constituent) The photopolymer constituent of this invention is useful although a transparent resistance image is formed especially, and it can consider various application. For example, application to the insulating layer used for a color filter-on array (COA) or a high aperture (HA) technique is explained based on drawing 1. The creation process of HA or the transparency wiring substrate model of COA is shown in drawing 1. As shown in A process, on transparency substrates, such as the well-known glass plate 11 or plastic film, such as a soda glass plate which has an oxidation silicon coat on a front face, a low-thermal-expansion-glass plate, a non alkali glass plate, and a quartz-glass plate, namely, by the usual approach by forming the thin film of a metal and nonmetals by sputtering and CVD of a semi-conductor, resistance, or a conductor, and combining photolithography The bottom ITO circuit pattern 12 for connecting the TFT array and them in a liquid crystal display is formed (Suzuki 82 work, a guide to liquid crystal display engineering, 28 pages - 36 pages, ***** 1998 issue).

[0074] Then, as shown in B process, the photosensitive thermosetting resin layer 13 is formed by spreading or the lamination on the substrate 11 with which the pattern 12 was installed. If required, well-known silane coupling down stream processing can be performed in order to improve adhesion with a substrate. As an example of a silane coupling agent, a trimethoxysilyl benzoic acid, gamma-methacryloxypropyl trimethoxy silane, vinyltriethoxysilane, vinyltrimethoxysilane, gamma-isocyanate propyl triethoxysilane, gamma-glycidyloxypropyltrimethoxysilane, beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, etc. can be mentioned.

[0075] By next, as shown in C process, UV exposure is carried out through the photo mask 14 for making a hole for interlayer connections called a contact hole in the appropriate location on the bottom ITO pattern which should be connected, in continuing D process, negatives are developed with an alkali developer, the exposure section is dissolved, and pattern 13A is formed. (Although the case of positive type sensitive material is illustrated here, in the case of a

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hydroxyacetic acid ethyl, 2-hydroxy-2-methyl-butane acid methyl, Ester, such as 3-methoxy methyl propionate, 3-methoxy ethyl propionate, 3-ethoxy methyl propionate, 3-ethoxy ethyl propionate, ethyl acetate, and butyl acetate, is mentioned. In these, diethylene glycols, such as ester; diethylene-glycol wood ether, such as ethylene glycol alkyl ether acetate; 2-hydroxy ethyl propionate, such as glycol ester; ethylcellosolve acetate, such as ethylene glycol wood ether, 3-methoxy methyl propionate, and 3-ethoxy ethyl propionate, can be used suitably.

[0080] Furthermore, N-methyl formamide, N,N-dimethylformamide, N-methylformamide, N-methyl acetamide, N,N-dimethylacetamide, N-methyl pyrrolidone, Dimethyl sulfoxide, benzyl ethyl ether, diethyl ether, Acetonylacetone, an isophorone, a caproic acid, a caprylic acid, 1-octanol, High boilers, such as 1-nonanol, benzyl alcohol, benzyl acetate, ethyl benzoate, oxalic acid diethyl, a diethyl maleate, gamma-butyrolactone, ethylene carbonate, propylene carbonate, and a phenyl cellosolve acetate, can also be added.

[0081] In these, diethylene glycols, such as ester, such as ethylene glycol alkyl ether acetate, such as glycol ester, such as ethylene glycol wood ether, and ethylcellosolve acetate, 2-hydroxy propylene acid ethyl, 3-methoxy methyl propionate, and 3-ethoxy ethyl propionate, and diethylene-glycol wood ether, can be suitably used in respect of the solubility of each component, and the ease of carrying out of formation of a paint film. These organic solvents are independent, or can use two or more kinds together, and can be used.

[0082] Moreover, in preparation of a spreading solution according to the constituent of this invention, the component of alkali fusibility resin [of this invention], 1, and 2-quinone diazide compound and others can be adjusted by dissolving at a predetermined rate into a predetermined solvent and/or its mixed liquor, for example. Use can also be presented with it after filtering the solution of this invention constituent using the micro barrier filter of 0.2 micrometers of apertures etc.

[0083] (Formation of a photosensitive paint film) using the positive type or negative-mold photopolymer constituent of this invention - for example, a positive type or a negative-mold photopolymer paint film can be formed on a base as follows.

(The applying method) The prepared positive type or negative-mold photopolymer constituent solution is applied to a substrate front face, by usually performing stoving in oven, a solvent is removed and the paint film of a photopolymer constituent is formed. Especially as the method of application of a constituent solution, it is not limited, for example, various kinds of approaches, such as a spray method, the roll coat method, the rotation applying method, the slit coat method, the extrusion coat method, the curtain coat method, the die coat method, the wire bar coat method, and the knife coat method, can be adopted. As conditions for prebaking, although it changes with the class of each component, operating rates, etc., it is usually for [30 seconds] - a 15-minute about room at 60-110 degrees C.

[0084] (A positive type or replica method of a negative-mold photopolymer imprint ingredient) Spreading desiccation of the positive type of this invention or the negative-mold photopolymer constituent solution is carried out on a temporary base material, and the laminating imprint of the sensitization layer is carried out under heating pressurization with a laminator on a base after forming a positive type or a negative-mold photopolymer layer imprint ingredient. The temperature of the heating sticking-by-pressure roll at the time of an imprint is conditions with 5 kg/cm² - 25 kg/cm² advantageous [the linear pressure at the time of sticking by pressure] at 50 degrees C - 150 degrees C. The rate of a lamination has the amount of desirable part [for 0.2m/-], and 4m/at a bearer rate. For heating sticking-by-pressure roll temperature, as especially desirable conditions, the linear pressure at the time of sticking by pressure is [10 kg/cm² - 15 kg/cm² and a bearer rate] parts for [for 1m/-], and 3m/at 130 degrees C - 140 degrees C.

[0085] (The formation approach of the resistance thin film pattern to a base top) Pattern formation is carried out by carrying out a development to the formed paint film using a developer, after carrying out an optical exposure through the mask of a predetermined pattern, and removing an optical exposure part or a non-irradiating part. As a light used here, for example g line (wavelength of 438nm), i line (wavelength of 355nm), and an ultrahigh pressure mercury lamp. The ultraviolet rays of the shape of the letter of continuation from the well-known light

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sources, such as a xenon LGT, a carbon arc lamp, and an argon laser, and/or the bright line, charged-particle lines, such as X-rays, such as far ultraviolet rays, such as a K α excimer laser, and a synchrotron radiation line, and an electron ray, are mentioned, and the ultraviolet rays of 300nm - 440nm field containing g line, i line, and these are mentioned as a desirable thing in these. Light transmittance with a wavelength of 400nm or more may use together like a publication the light filter which is 2% or less to JP.6-59119A.

[0086] As a developer of the above-mentioned photopolymer layer, although the thin water solution of an alkaline substance is used, what carried out little addition of water and the organic solvent of a miscibility may be used further, as a suitable alkaline substance — alkali-metal hydroxides (an example and a sodium hydroxide —) A potassium hydroxide and alkali-metal carbonates (an example, a sodium carbonate, potassium carbonate) Alkali-metal bicarbonates (an example, a sodium hydrogencarbonate, potassium hydrogencarbonate) Alkali-metal silicates (an example, a sodium silicate, potassium silicate) Alkali-metal metasilicates (an example, a meta-sodium silicate, meta-potassium silicate) Ammonia, ethylamine, n-propylamine, diethylamine, triethylamine, methyl diethylamine, dimethylethanamine, triethanolamine, diethanolamine, monoethanolamine, a morpholine and tetra-alkyl AMMONIUM hydroxide (for example, tetramethylammonium hydroxide —) A tetraethylammonium hydroxide, pyrrole, piperidine, 1, 8-diazabicyclo [5, 4, 0]-7-undecene, 1, and 5-diazabicyclo [4, 3, 0]-5-nonane or trisodium phosphate can be mentioned. The concentration of an alkaline substance is 0.01 mass % - 30 mass %, and, as for pH, 8-14 are desirable.

[0087] moreover, as the above-mentioned water and a suitable organic solvent with a miscibility A methanol, ethanol, 2-propanol, 1-propanol, a butanol, Diacetone alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, Ethylene glycol mono-n-butyl ether, benzyl alcohol, An acetone, a methyl ethyl ketone, a cyclohexanone, epsilon-caprolactone, Gamma-butyrolactone, dimethylformamide, dimethylacetamide, hexamethylphosphoramide, ethyl lactate, methyl lactate, epsilon caprolactam, and N-methyl pyrrolidone can be mentioned. The concentration of water and the organic solvent of a miscibility has common 0.1 mass % - 30 mass %.

[0088] A still better known surfactant can be added in a developer. The concentration of a surfactant has desirable 0.01 mass % - 10 mass %. A developer can be used also as spray liquid also as bath liquid. Furthermore, as the development approach, a liquid peak method, a dipping method, rocking dip coating, a spray method, etc. can be used.

[0089] In order to remove development Society for Cutting Up Men of an exposure part, the method of using the atomizing pressure at the time of spraying approaches, such as grinding against the rotation brush in a developer, or grinding against humid sponge, or a developer is desirable. The temperature of a developer usually has the desirable range of 40 degrees C from near a room temperature. It is also possible to put in a rinsing process after a development.

[0090] the thin film by which patterning was carried out after the development — receiving — for example, a stream — rinse processing by washing is performed. Moreover, decomposition processing of 1 which remains in the thin film concerned, 2-quinone JLAJTO compound, etc. is performed by irradiating the radiation by the ultrahigh pressure mercury lamp, electron-beam-irradiation equipment, etc. on the whole surface. Hardening processing of the thin film concerned is performed by calcinating this thin film with heating apparatus, such as a hot plate and oven. The burning temperature in this hardening processing is 150-250 degrees C, and firing time is for 5 - 90 minutes (for [in calcinating on a hot plate, when calcinating in 5 - 30 minutes, and in oven] 30 - 90 minutes). Thus, the thin film excellent in solvent resistance and transparency can be formed on the front face of a substrate.

[0091] (The manufacture approach of a positive type or a negative-mold photopolymer imprint ingredient) In order to produce a positive type or a negative-mold photopolymer layer imprint ingredient using the positive type or negative-mold photopolymer constituent of this invention, it carries out by coating of the positive type which usually dissolved in the solvent on the film made from plastics of transparency, or a negative-mold photopolymer constituent (the example of a positive type is shown in drawing 2).

[0092] Usually, spreading desiccation of a direct positive mold or the negative-mold

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polymer 80 degrees C or more, and to lower substantial softening temperature to 80 degrees C or less. Moreover, in order to adjust adhesive strength with a temporary base material in these organic high polymers, it is possible to add various kinds of polymers in the range in which substantial softening temperature does not exceed 80 degrees C, the supercooling matter, an adhesion amelioration agent or a surfactant, a release agent, etc. As an example of a desirable plasticizer, a polypropylene glycol, a polyethylene glycol, dioctyl phthalate, diheptylphthalate, dibutyl phthalate, tricresyl phosphate, and cresyl-diphenyl-phosphate biphenyl diphenyl phosphate can be mentioned. The thickness of a thermoplastics layer has desirable 6 micrometers or more. It becomes difficult to absorb the irregularity of a substrate 1 micrometers or more completely as the thickness of a thermoplastics layer is 5 micrometers or less. Moreover, about an upper limit, about 100 micrometers or less are common from development nature and manufacture fitness, and about 50 micrometers or less are desirable.

[0099] inconvenient [between the purpose of the oxygen cutoff at the time of exposure, a thermoplastics layer, and a photopolymer layer] as an interlayer — it is mixed and is prepared for the purpose of prevention. It distributes or dissolves in water or an alkali water solution, and an interlayer can use a well-known thing that what is necessary is just what shows low oxygen permeability. For example, polyvinyl ether / maleic-anhydride polymer given in JP.46-2121A or JP.56-40824.B. The water-soluble salt of carboxy alkyl cellulose, and water-soluble cellulose ether The salt of carboxy alkyl starch, a monohydrate, polyvinyl alcohol, a polyvinyl pyrrolidone. Various kinds of polyacrylamides, various kinds of water-soluble polyamides, the water-soluble salt of polyacrylic acid, Two or more sorts of these combination can be mentioned to the water-soluble salt of a group which consists of gelatin, an ethyleneoxide polymer, various kinds of starch, and its prototype, the copolymer of styrene/maleic acid, and a MAREINETO resin pan. Especially, the combination of polyvinyl alcohol and a polyvinyl pyrrolidone is desirable. The content of a polyvinyl pyrrolidone has common 1 - 75 mass % of an oxygen filter layer solid, that [polyvinyl alcohol's] whose saponification value is more than 80 mol % is desirable, and it is [1 - 60 mass % is desirable, and] ten to 50 mass % especially. Under by 1 mass %, if sufficient adhesive property with a photopolymer layer is not acquired but 75 mass % is exceeded, oxygen cutoff ability will fall. The thickness of an oxygen filter layer is very thin, and its 0.5-2 micrometers are especially desirable about 0.1-5 micrometers. In less than about 0.1 micrometers, if the permeability of oxygen is too high and exceeds about 5 micrometers, it will take time amount too much at the time of development or oxygen filter layer removal. The above-mentioned positive type or a negative-mold photopolymer layer can be formed on this middle class, and the multilayer positive type of this invention or a negative-mold photopolymer layer imprint ingredient can be obtained.

[0100] In order to avoid the impurity adhesion and damage in the case on storage, as for a protection film, it is desirable to prepare a thin protection film. Although a protection film is the same as a temporary base material or may consist of a similar ingredient, it must dissociate from a positive type or a negative-mold photopolymer layer easily. Moreover, the smooth nature of the field which carries out a laminating to a positive type or a negative-mold photopolymer layer is important, and since it will become the damage to a photopolymer layer if there is a projection it is [projection] about 0.1 micrometers, it becomes a problem. As such an ingredient, for example, silicone paper, polyolefine, or a poly tetrafluoroethylene sheet is desirable. They are a polypropylene film or a polyethylene film especially preferably. As for the thickness of a protection film, it is desirable that it is about 5-100 micrometers. It is 7 micrometers - 15 micrometers especially preferably.

[0101]

[Example] Hereafter, although the example of this invention is explained in full detail, this invention is not limited to these examples. In addition, especially, as long as there is no notice, the "mass section" and "mass %" are expressed altogether the "section" in this example, and "%".

[0102] The [example 1 of raw material composition] isocyanate ethyl methacrylate 108.6 section is dissolved in the desiccation ethyl-acetate 108.6 section. The tin dioctylate 0.1 section and the G t-octyl hydroquinone 0.01 section are added here. The methanol 100.0 section is dropped

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photopolymer layer (or photosensitive heat-curing resin layer) 22 is carried out on the temporary base materials 21, such as a polyethylene terephthalate film of 5 micrometers - 30 micrometer thickness, and the positive type of a configuration of having stuck the protection film 23 on this positive type or the negative-mold photopolymer layer by the case or a negative-mold photopolymer layer imprint ingredient can be formed.

[0093] (A multilayer positive type or the manufacture approach of a negative-mold photopolymer layer imprint ingredient) On the other hand, the imprint ingredient of the multilayer configuration corresponding to the problem which air bubbles generate between a substrate and a photosensitive layer at the time of an imprint for the irregularity of a substrate is known by JP.2794242 and JP.10-97061A (drawing 3). For example, as having been indicated by JP.10-97061A, by the same approach, the alkali fusibility thermoplastics layer 32 and the middle class 33 are formed in temporary base material top 31, and the multilayer positive type or negative-mold photopolymer imprint ingredient which it was applied in order of the positive type or this invention or the negative-mold photopolymer layer (or photosensitive heat-curing resin layer) 34, and the protection film 35 laminated on it further can also be used suitably.

[0094] The above spreading solutions were created, the alkali fusibility thermoplastics layer and the interlayer were applied upwards on the temporary base material, and spreading desiccation of a positive type or the negative-mold photopolymer layer is carried out by the thickness according to the purpose. The thickness of a photopolymer layer has the desirable range of 0.1-20 micrometers. Only the hardening film in which resistance is inferior may be able to be made from less than 0.1 micrometers. If it exceeds 20 micrometers, problems, such as a fall of development nature and a fall of image repeatability, may occur. The thickness of this positive type or a negative-mold photopolymer layer can be set as arbitration according to the need for each function in the above-mentioned range.

[0095] For example, when using it as a projection pattern for orientation division of the above, it is 0.5 micrometers - 5 micrometers, and 2 micrometers - 4 micrometers are especially desirable. Moreover, the thickness when using it as an insulator layer used for the color filter of the aforementioned COA method or a high aperture method is optimized according to the dielectric constant of the thin film after hardening by 0.5 micrometers - 5 micrometers.

[0096] It is desirable to have an alkali fusibility thermoplastics layer and good detachability as a temporary base material, and to consist of flexible matter stably chemically and thermally. Specifically, thin sheets or such laminated material, such as Teflon (trademark), polyethylene terephthalate, polyethyleneterephthalate, polyarylate, a polycarbonate, polyethylene, and polypropylene, are desirable. In order to acquire good detachability, as for surface preparation, such as glow discharge, it is common not to carry out and not to prepare undercoat, such as gelatin, either, 5-300 micrometers is suitable for the thickness of a temporary base material, and 10 micrometers - especially its 150 micrometers are desirable. In 5 micrometers or less, since the tensile strength at the time of a lamination runs short, it is extended and inconvenient Siwa enters. The rate of a lamination is not raised in order that heat conduction of a heat lamination may be overdue, if thicker than 300 micrometers.

[0097] As for the resin which constitutes an alkali fusibility thermoplastics layer, it is desirable that substantial softening temperature is 80 degrees C or less. Softening temperature as thermoplastics of alkali fusibility 80 degrees C or less The saponification object of ethylene and an acrylic ester copolymer, the saponification object of styrene and an acrylic ester (meta) copolymer. The saponification object of vinyltoluene and an acrylic ester (meta) copolymer. Saponification objects, such as acrylic ester (meta) copolymers, such as Pori (meta) acrylic ester and (meta) butyl acrylate, and vinyl acetate, since — although it is desirable that at least one is chosen — further — "a plastics engine-performance handbook" (Japan Plastics Industry Federation —) The softening temperature by the work edited by the all Japan plastic-molding industrial union meeting, the Kogyo Chosakai Publishing issue, and October 25, 1968 issue can use a meltable thing for an alkali water solution among organic macromolecules about 80 degrees C or less.

[0098] Moreover, it is able for softening temperature to add various kinds of plasticizers which have this high polymer and compatibility in the organic high polymer also in an organic high

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stirring at a room temperature, and it stirs at a room temperature further for 3 hours. The compound (block isocyanate 1) 130.7 section which blocked this reaction mixture with the sodium-hydrogencarbonate water solution by washing and rinsing further and carrying out concentration hardening by drying 1%, and blocked the isocyanate radical of isocyanate ethyl methacrylate with the methanol was obtained.

[0103] The [example 2 of raw material composition] isocyanate ethyl methacrylate 77.6 section is dissolved in the desiccation ethyl-acetate 77.6 section. The tin dioctylate 0.1 section and the G t-octyl hydroquinone 0.01 section are added here. The solution which dissolved the phenol 70.6 section in the desiccation ethyl-acetate 70.6 section is dropped stirring at a room temperature, and it stirs at a room temperature further for 3 hours. The compound (block isocyanate 2) 80.8 section which blocked this reaction mixture with the sodium-hydrogencarbonate water solution by washing and rinsing further and carrying out concentration hardening by drying 1%, and blocked the isocyanate radical of isocyanate ethyl methacrylate with the phenol was obtained.

[0104] The 24.5 sections and the cyclohexyl methacrylate 17.6 section (a presentation ratio is 28:40:32) were dissolved for the block isocyanate 1 obtained in the [synthetic example 1] methacrylic-acid 7.9 section and the example 1 of raw material composition in the methoxy propyl acetate 150.0 section. Heating stirring of this solution is carried out under 70 degrees C and a nitrogen air current, the V-65 (Wako Pure Chem 2, 2'-azobis - (2, 4-dimethylvaleronitrile)) 0.57 section is added, and heating stirring is carried out at 70 degrees C for 4 hours. It heated at 80 more degrees C for 1 hour, and the methoxy propyl acetate solution of a copolymer was obtained. The n-hexane 1500 section was filled with this solution under churning, the polymer was deposited, the obtained solid-state polymer was separated, and the copolymer 1 was obtained by drying. The mass mean molecular weight (polystyrene conversion) was 32000.

[0105] The copolymer 2 was obtained like the synthetic example 1 except making into the 18.3 sections and the benzyl methacrylate 23.0 section (a presentation ratio being 30:30:40) block isocyanate 1 which obtained the raw material monomer in the example 1 of the [synthetic example 2] composition in the methacrylic-acid 8.4 section and the example 1 of raw material composition. The mass mean molecular weight (polystyrene conversion) was 29000.

[0106] The 28.0 sections and the cyclohexyl methacrylate 15.2 section (a presentation ratio is 28:40:32) were dissolved for the block isocyanate 2 obtained in the [synthetic example 3] methacrylic-acid 6.8 section and the example 2 of raw material composition in the methoxy propyl acetate 75.0 section. Heating stirring of this solution is carried out under 70 degrees C and a nitrogen air current, the V-65 (Wako Pure Chem 2, 2'-azobis - (2, 4-dimethylvaleronitrile)) 0.48 section is added, and heating stirring is carried out at 70 degrees C for 4 hours. It heated at 80 more degrees C for 1 hour, and the methoxy propyl acetate solution of a copolymer was obtained. The n-hexane 1000 section was filled with this solution under churning, the polymer was deposited, the obtained solid-state polymer was separated, and the copolymer 3 was obtained by drying. The mass mean molecular weight (polystyrene conversion) was 48000.

[0107] The copolymer 4 was obtained like the synthetic example 3 except making into the 21.1 sections and the benzyl methacrylate 19.8 section (a presentation ratio being 30:30:40) block isocyanate 2 which obtained the raw material monomer in the example 3 of the [synthetic example 4] composition in the methacrylic-acid 7.3 section and the example 2 of raw material composition. The mass mean molecular weight (polystyrene conversion) was 49000.

[0108] The [example 1 of comparison composition] m-xylylene diisocyanate 94.1 section is dissolved in the desiccation ethyl-acetate 94.1 section. The methanol 180.0 section is dropped stirring at a room temperature. Furthermore, it stirs at a room temperature for 4 hours, and the white solid-state which deposits is carried out a ** exception. The compound 61.3 section which blocked the isocyanate radical of m-xylylene diisocyanate with the methanol by ****ing the obtained individual from ethyl acetate/hexane was obtained.

[0109] The [example 2 of comparison composition] isophorone diisocyanate 68.7 section is dissolved in the desiccation ethyl-acetate 68.7 section. After adding the tin dioctylate 0.1 section, the solution which dissolved the phenol 67.8 section in the desiccation ethyl-acetate 67.8 section is dropped stirring at a room temperature. Furthermore, it stirs at a room

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temperature for 4 hours, and the white solid-state which deposits is carried out a ** exception.

The compound 95.0 section which blocked the isocyanate radical of isophorone diisocyanate with the phenol by **** was the obtained individual from ethyl acetate/hexane was obtained.

[0110] The tin dioctylate 0.05 section is added in the 50wt% ethyl-acetate solution ("bamboo NETO D-212" by Takeda Chemical Industries, Ltd.) 209 section of the isocyanate object of (example 3 of comparison composition) toluene diisocyanate. The methanol 100 section is dropped stirring a solution at 40 degrees C. It stirs at 40 more degrees C. Vacuum concentration of the reaction mixture was carried out, and the compound 131.0 section which blocked the isocyanate radical of the isocyanate object of toluene diisocyanate with the methanol by drying the white solid-state which adds a hexane and deposits a ** exception was obtained.

[0111] Manufacture of a (example 1) negative-mold photosensitivity solution, and formation of an insulating layer (the applying method for high aperture method insulator layers)

The 27 mass % propylene-glycol-monomethyl-ether acetate solution 100 mass section of the copolymer 1 obtained in the synthetic example 1, The dipentaerythritol hexaacrylate 6.3 mass section, and the 4-bis(TORIKURORO methyl)-6-(N and N-diethoxy carbonylmethylamino)-BUROMO phenyl)-s-triazine 0.41 mass section, The fluorochemical surfactant F176PF(Dainippon Ink make) 0.25 mass section and the 0.0225 mass section of the Victoria PYUA blue BOH are dissolved in a mixed solution from the propylene-glycol-monomethyl-ether acetate 126 mass section and the methyl-ethyl-ketone 63 mass section. The negative-mold photosensitivity (heat curing) resin solution C1 was obtained.

[0112] It applied on the glass substrate which has the wiring putter of TFT and ITO with a rotating type spreading machine, and the paint film which does not have tackiness in the front face of 4micro thickness after desiccation was obtained. It had a black hole pattern in inside transparent to this, and in piles, 30 mJ/cm² was exposed with 2kW ultrahigh pressure mercury lamp, and the photo mask which is the test chart which has the bore diameter of size variously was developed with the spray developing machine using the 1 mass % monoethanolamine water solution. It heated in 200-degree C oven after that for 30 minutes.

[0113] The bore diameter by which the obtained insulating-layer image was resolved was 10 micrometers, and did not have a development residual membrane, and its slope was [the hole configuration] as good as 27 degrees (development nature is good). Moreover, the thickness change after BEKU is -20% in front of BEKU, and thermal resistance was excellent. Permeability was 97% on the wavelength of 350nm.

[0114] On this insulator layer, the ITO film of 0.2-micrometer thickness was obtained by the sputter. Coat besides with the ITO etching resist of a commercial positive type, and after drying Although it was immersed in the exfoliation liquid which consists of dimethyl sulfoxide and monoethanolamine (mass ratio 3:7) for 10 minutes and ITO etching resist was exfoliated at 80 degrees C after removing the part which is not covered with an ITO resist by after exposure and acid etchant through a mask The insulating layer of a substrate carried out neither swelling nor exfoliation, but its adhesion of ITO was also good (exfoliation liquid resistance is good).

[0115] Moreover, the fact that adhesion with bottom ITO wiring of the bottom of the contact hole of obtained upper ITO was also excellent shows that there is no development residual membrane of this ingredient (development nature is good). Moreover, this negative-mold photosensitivity (heat curing) resin solution is sealed in a container, when change of viscosity is measured after neglect for four days at 50 degrees C, it is completely changeless, and it was admitted that there was no change also in development nature (coating liquid passage-of-time stability is good).

[0116] Except having changed the copolymer 1 in the (example 2) example 1 into the copolymer 2, the photopolymer constituent was created like the example 1 and it evaluated similarly. A result is shown in Table 1.

[0117] The copolymer 1 in the (examples 1-2 of comparison) example 1 was changed into the copolymer (copolymerization mole ratio 28/72, mass average-molecular-weight ** 30,000) of a methacrylic acid / methacrylic-acid benzyl ester, and except having newly added the example 1 of comparison composition, or the compound 6.3 mass section of 2, the photopolymer constituent was created like the example 1 and it evaluated similarly. A result is shown in Table

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stratification: The copolymer 1 of C3) and the synthetic example 1 35.7 The section and dipentaerythritol hexaacrylate 13.4 The section, 2, 4-bis(TORIKURORO methyl)-6-[4-(N and N-diethoxy carbonylmethylamino)-3-BUROMO phenyl]-s-triazine 1.32 The section and the hydroquinone monomethyl ether 0.02 The section and F176PF (Dainippon Ink surface active agent) 0.09 The section and propylene-glycol-monomethyl-ether acetate 400 The section and methyl ethyl ketone 500 Section [0127] R, G, B, and the imprint ingredient for black matrices were formed by (2 micrometers of desiccation thickness [Respectively]) using each coating liquid of each coating liquid presentation for sensitization stratification of the following table 2 (weight section), applying on the sheet which applied the thermoplastics layer and interlayer on the above-mentioned temporary base material, and drying on the glass substrate (0.7mm in thickness) in which wiring which serves as a TFT array from under ITO was formed. Using these, on the bottom ITO substrate, the black matrix of 1.8 micrometers of thickness, R and G which opened the contact hole of 30 tilt angles in each pixel in the size of 20 micrometers, and B pixels were formed, respectively, and the color filter was produced by imprint pattern exposure, development, and BEKU.

[0128]

[Table 2]

材料名	R	G	B	K
ペンタエリトールヘキサアクリレート	1.34	3.28	2.18	1.8
2-エチルヘキシルアセテート				1.8
メチルエチルケトン				
フッ素系表面活性剤				
プロピレングリコールモノメチルエーテルアセテート	3.75	4.01	3.99	2.7
2-エチルヘキシルアセテート	0.31	0.19	0.2	0.14
1, 3, 4-オキサジナール	1.89	1.29	0.25	
7-(2-(4-(3-ヒドロキシメチル)-3-フェニルメチル)-6-エチルアミノ)トリアジン	0.07	0.13	0.12	0.09
フッ素系表面活性剤	0.03	0.004	0.02	0.02
レジストコート	24.7			
レジストコート		18.9		
レジストコート			18.1	
レジストコート				43.9
レジストコート				3.5
レジストコート	35.5	12.8	7.8	40
レジストコート	30	39.9	39.5	60

[0129] The laminating of the negative-mold photosensitivity (heat curing) resin layer front face was carried out in piles using the laminator after removing a covering sheet from the aforementioned multilayer negative-mold photosensitivity (heat curing) resin stratification ingredient on the color filter which has the above-mentioned black matrix and the pixel of R, G, and B, and UV exposure of 300 mJ/cm² was performed for the photo mask which has a contact hole pattern for insulating stratification after removing a temporary base material in piles.

[0130] Dissolution removal of a thermoplastics layer and the interlayer was carried out using the 1 mass % triethanolamine water solution. Under the present circumstances, the negative-mold photosensitivity (heat curing) resin layer was not developed substantially. Subsequently, BEKU [the dose of 1000 mJ/cm²] in whole surface UV Mitsuetsu putting and 180-degree C oven for 1 hour after developing negatives by removing an unexposed part using a 1 mass % monoethanolamine water solution.

[0131] The thickness of the insulating layer which is a negative-mold photosensitivity (heat curing) resin layer by which was exposed completely and heat-curing processing was carried out

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1.

[0118] Except having changed the compound of the example 1 of comparison composition in the example 1 of the [example 3 of comparison] comparison into pentaerythritol polyglycidyl ether, the photopolymer constituent was created like the example 1 of a comparison, and it evaluated similarly. A result is shown in Table 1.

[0119] Except not using the compound of the example 1 of comparison composition in the example 1 of the [example 4 of comparison] comparison, the photopolymer constituent was created like the example 1 of a comparison, and it evaluated similarly. A result is shown in Table 1.

[0120] A (evaluation basis) and development nature — 15micro or less of definition and a thing without the development remainder were made into O.

— Thermal resistance — The thickness change after heat treatment made 30% or less O, and made ** and more than it x for 50% or less.

— Exfoliation liquid resistance — What is swollen although O and exfoliation do not carry out what does not swell and exfoliate was made into **, and what exfoliating was made into x.

— Coating liquid passage-of-time stability — The time amount which O and development take that where after neglect does not have change in development nature made x that to which ** and development become improper about what an increment or the development remainder produces for four days at 50 degrees C.

[0121]

[Table 1]

材料名	熱抵抗	耐熱性	剥離液抵抗	塗液安定性
例1	O	O	O	O
例2	O	O	O	O
例3	O	A	x	x
例4	O	O	O	x
例5	O	A	x	O

[0122] [Example 3] On creation of a multilayer negative-mold photosensitivity (heat curing) resin layer imprint ingredient, and the temporary base material with an insulating stratification thickness [to a color filter top] of 100 micrometers of a polyethylene terephthalate film, the coating liquid which consists of the following presentation H1 was applied and dried, and the thermoplastics layer whose desiccation thickness is 12 micrometers was prepared.

[0123]

The presentation of the coating liquid for < thermoplastics stratification: H1) and methyl methacrylate / 2-ethylhexyl acrylate/Benzyl methacrylate / methacrylic-acid copolymer (copolymerization mol presentation ratio =55/11.7/4.5/28.8, mass average-molecular-weight = 80000) The 15.0 sections and BPE-500 (polyfunctional acrylate made from New Nakamura Chemistry) The 7.0 sections and F177P (Dainippon Ink fluorochemical surfactant) The 0.3 sections and a methanol The 30.0 sections and methyl ethyl ketone The 19.0 sections and 1-methoxy-2-propanol The 10.0 sections [0124] Next, on the above-mentioned thermoplastics layer, the coating liquid which consists of the following presentation B1 was applied and dried, and desiccation thickness prepared the interlayer of 1.6-micrometer thickness.

presentation [of the coating liquid for < middle class formation : — B1) and polyvinyl alcohol ("PVA205" saponification degree:80-mol %) [by Kuraray Co., Ltd.] 130 sections - Polyvinyl pyrrolidone ("K-30" by the GAF corporation company) 60 sections - Distilled water 2110 sections - Methanol The 1750 sections [0125] On the temporary base material which has the above-mentioned thermoplastics layer and an interlayer, the photosensitive coating liquid of the following presentation C3 was applied and dried, the photopolymer layer whose desiccation thickness is 4 micrometers was formed, further, the covering sheet of polypropylene (12 micrometers in thickness) was stuck by pressure on this photopolymer layer, and the multilayer negative-mold photosensitivity (heat curing) resin layer imprint ingredient was produced.

[0126]

The presentation of the coating liquid for < negative-mold photosensitivity insulation

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was 3.3micro, and the pencil degree of hardness was 6H. The size of a bottom of the configuration of the contact hole section was mortar-like [with a tilt angle good at 30 degrees] in 13 micrometer (development nature is good). Moreover, it was substantially transparent and colorless and light transmittance was 95% on the wavelength of 350nm. The sputter of ITO was performed from besides and the transparent conductive layer of 0.2-micrometer thickness was formed.

[0132] Besides carry out spreading desiccation of the photoresist, and the mask which has the pattern of a transparent electrode is exposed in piles. The ITO part which is not covered with the resist after development by acid etchant after etching Dimethyl sulfoxide and the mixed solution of monoethanolamine (mass ratio 3:7) are used. When the photoresist was exfoliated by being immersed for 10 minutes at 80 degrees C, the photoresist exfoliated, there is also no peeling of ITO in an insulating layer, and the damage on Siwa by swelling etc. was not accepted in it, either (exfoliation liquid resistance is good). Moreover, in this multilayer negative-mold photosensitivity (heat curing) resin layer imprint ingredient, although processing same after neglect for four days was performed at 50 degrees C, it was admitted that there was no change in engine performance, such as development nature, (stability with the passage of time is good).

[0133] Except having changed the copolymer 1 in the coating liquid C3 of the (example 4) example 3 into the copolymer 3, the multilayer negative-mold photosensitivity (heat curing) resin layer imprint ingredient was created like the example 3, and processing and evaluation were performed similarly. Development nature, exfoliation liquid resistance, and stability with the passage of time were good like the example 3.

[0134] The copolymer 1 in the coating liquid C3 of the (example 5 of comparison) example 3 was changed into the copolymer (copolymerization mole ratio 28/72, mass average-molecular-weight ** 30,000) of a methacrylic acid / methacrylic-acid benzyl ester, and except having newly added the compound 13.4 mass section of the example 1 of comparison composition, the multilayer negative-mold photosensitivity (heat curing) resin layer imprint ingredient was created like the example 3, and it evaluated similarly. Although development nature was good, when exfoliating the photoresist for the pattern formation of a transparent electrode, peeling of ITO based on the swelling of an insulating layer was accepted partly (poor exfoliation liquid resistance).

[0135] Except having changed the compound of the example 1 of comparison composition in the example 5 of the (example 6 of comparison) comparison into pentaerythritol polyglycidyl ether, the multilayer negative-mold photosensitivity (heat curing) resin layer imprint ingredient was created like the example 5 of a comparison, and it evaluated similarly. Although development nature and exfoliation liquid resistance were good, when processing same after neglect for four days was performed at 50 degrees C, development was impossible on this multilayer negative-mold photosensitivity (heat curing) resin layer imprint ingredient (poor stability with the passage of time).

[0136] Except not using the compound of the example 1 of comparison composition in the example 5 of the (example 7 of comparison) comparison, the multilayer negative-mold photosensitivity (heat curing) resin layer imprint ingredient was created like the example 5 of a comparison, and it evaluated similarly. Although development nature was good, when exfoliating the photoresist for the pattern formation of a transparent electrode, peeling of ITO based on the swelling of an insulating layer was accepted (poor exfoliation liquid resistance).

[0137] Manufacture of a (example 5) positive type photosensitivity solution, and formation of an insulating layer (the applying method for high aperture method insulator layers)

21 mass sections of the copolymer 1 of the synthetic example 1 are dissolved in the mixed solution of the propylene-glycol-monomethyl-ether acetate 30 mass section and the methyl-ethyl-ketone 13 mass section, and it is 1 and 2-naphthoquinonediazide, - 5 - The sulfonic-acid-4-tert-octyl phenyl ester 10 mass section and the fluorochemical surfactant F176PF(Dainippon Ink make) 0.25 mass section were dissolved, and the positive type photosensitivity (heat curing) resin solution C5 was obtained.

[0138] It applied on the glass substrate which has the wiring putter of TFT and ITO with a rotating type spreading machine, and the paint film which does not have tackiness in the front face of 2micro thickness after desiccation was obtained. In piles, 600 mJ/cm² was exposed with

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2kW ultrahigh pressure mercury lamp, and the photo mask which is the test chart which has various bore diameters in this was developed with the spray developing machine using the 1 mass % monoethanolamine water solution. The ultrahigh pressure mercury lamp was used for the whole surface after that, and it exposed with the quantity of light of 1000 mJ/cm², and heated in 200-degree C oven after that for 30 minutes.

[0139] The bore diameter by which the obtained insulating-layer image was resolved was 4 micrometers, and did not have a development residual membrane, and its slope was [the hole configuration] as good as 23 degrees (development nature is good). Moreover, the thickness change after BEKU is -28% in front of BEKU, and thermal resistance was excellent (thermal resistance is good). Permeability was 97% on the wavelength of 350nm.

[0140] On this insulator layer, the ITO film of 0.2-micrometer thickness was obtained by the sputter. Although it was immersed in the exfoliation liquid which consists of monoethanolamine and dimethyl sulfoxide (mass ratio 7:3) for 10 minutes and ITO etching resist was exfoliated at 80 degrees C after coating besides with the ITO etching resist of a commercial positive type and removing the part which is not covered with an ITO resist by acid etchant after exposure through the mask after drying, the insulating layer of a substrate did not carry out swelling, either, but its adhesion of ITO was also good (exfoliation liquid resistance is good).

[0141] Moreover, since adhesion with bottom ITO wiring of the bottom of the contact hole of obtained upper ITO was also excellent, it turns out that there is no development residual membrane of this ingredient (development nature is good). When this positive type photosensitivity (heat curing) resin solution was sealed in the container and change of viscosity was measured after neglect for four days at 50 degrees C, it was admitted that there was no change also in ** which is completely changeless, and development nature (coating liquid passage-of-time stability is good).

[0142] Except changing the copolymer 1 of the [example 6] example 5 into a copolymer 4, like the example 5, the positive type photosensitivity (heat curing) resin solution was created, and processing and evaluation were performed similarly. Development nature, exfoliation liquid resistance, and stability with the passage of time were good like the example 5.

[0143] The copolymer 1 in the [example 8 of comparison] example 5 was changed into the copolymer (copolymerization mole ratio 28/72, mass average-molecular-weight ** 30,000) of a methacrylic acid / methacrylic-acid benzyl ester, and except newly adding the compound 10.0 mass section of the example 3 of comparison composition, the positive type photosensitivity (heat curing) resin solution was created like the example 5, and it evaluated similarly. When development nature fell a little (definition is 10micro) and the photoresist for the pattern formation of a transparent electrode was exfoliated, peeling of ITO based on the swelling of an insulating layer was accepted partly (poor exfoliation liquid resistance).

[0144] Except changing the compound of the example 3 of comparison composition in the [example 9 of comparison] comparison into pentaerythritol polyglycidyl ether, like the example 8 of a comparison, the positive type photosensitivity (heat curing) resin solution was created, and it evaluated similarly. Although it was good, development nature and exfoliation liquid resistance sealed this positive type photosensitivity (heat curing) resin solution in the container, when they measured change of viscosity after neglect for four days at 50 degrees C, they were thickening it, and were not able to be applied (poor coating liquid passage-of-time stability).

[0145] [Example 7] Creation of a multilayer positive type photosensitivity (heat curing) resin layer imprint ingredient, and insulating stratification to a color filter top (COA replica method) On the temporary base material with a thickness of 100 micrometers of a polyethylene terephthalate film, the coating liquid H1 for thermoplastics stratification used in the example 3 was applied and dried, and the thermoplastics layer whose desiccation thickness is 20 micrometers was prepared. Next, on the above-mentioned thermoplastics layer, the coating liquid B1 for interlayer formation used in the example 3 was applied and dried, and desiccation thickness prepared the interlayer of 1.6-micrometer thickness. On the temporary base material which has the above-mentioned thermoplastics layer and the middle class, the positive type photosensitivity coating liquid of the following presentation C7 was applied and dried, the

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the photoresist for the pattern formation of a transparent electrode, peeling of ITO based on the swelling of an insulating layer was accepted partly (poor exfoliation liquid resistance).

[0152] Except changing the compound of the example 1 of comparison composition in the example 10 of the [example 11 of comparison] comparison into a novolak mold epoxy resin, like the example 10 of a comparison, the multilayer positive type photosensitivity (heat curing) resin layer imprint ingredient was created, and it evaluated similarly. Although exfoliation liquid resistance was good, development nature was falling a little (definition falls to 12micro).

Moreover, about this multilayer positive type photosensitivity (heat curing) resin layer imprint ingredient, when processing same after neglect for four days was performed at 50 degrees C, development was impossible (poor stability with the passage of time).

Except not using the compound of the example 1 of comparison composition in the example 10 of the [example 12 of comparison] comparison, the multilayer positive type photosensitivity (heat curing) resin layer imprint ingredient was created like the example 10 of a comparison, and it evaluated similarly. Although development nature was good, when exfoliating the photoresist for the pattern formation of a transparent electrode, peeling of ITO based on the swelling of an insulating layer was accepted (poor exfoliation liquid resistance).

[Effect of the Invention] According to this invention, also in which photopolymer constituent of a positive type or a negative mold especially a photosensitive heat-curing resin constituent or a photopolymer layer imprint ingredient, especially a photosensitive heat-curing resin layer imprint ingredient, the photopolymer constituent or imprint ingredient which the development by the weak alkaline developer was possible, whose resolution was high, and the pattern excellent in the exfoliation liquid resistance after heat-curing processing was obtained, and was excellent also in the stability of a sensitized material with the passage of time can be offered.

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photopolymer layer whose desiccation thickness is 2 micrometers was formed, further, the covering sheet of polypropylene (12 micrometers in thickness) was stuck by pressure on this photopolymer layer, and the multilayer positive type photosensitivity (heat curing) resin layer imprint ingredient was created.

[0146]

The presentation of the coating liquid for < positive type photosensitivity thermosetting stratification: The copolymer 1 of C7) and the synthetic example 1 The 21.0 sections and propylene-glycol-monomethyl-ether acetate 1 The 30.0 sections, 2 - Naphthoquinonediazide-5-sulfonic-acid 4-tert-octyl phenyl ester The 10.0 sections and fluorochemical surfactant F176PF (Dainippon Ink make) The 0.25 sections and the Victoria PYUA blue BOM The 0.225 sections, 2, 4-bis[4-(2,6-dimethyl-4-pyridyl)-2-methyl-5-phenyl-1,3,4-oxadiazole]methane The 13.0 sections [0147] The black matrix of 1.8 micrometers of thickness, R and G which opened the contact hole of 30 μm angles in each pixel in the size of 20 micrometerphi, and B pixels were formed on the bottom ITO substrate like the example 3, and the color filter was created. The laminating of the positive type photosensitivity (heat curing) resin layer front face was carried out in piles using the laminator after removing a covering sheet from a positive type photosensitivity (heat curing) resin stratification ingredient on the color filter which has the above-mentioned black matrix and the pixel of R, G, and B, and UV exposure of 300 mJ/cm² was performed for the photo mask which has a contact hole pattern for insulating stratification after removing a temporary base material in piles. Dissolution removal of a thermoplastics layer and the interlayer was carried out using the 1 mass % triethanolamine water solution. Under the present circumstances, the positive type photosensitivity (heat curing) resin layer was not developed substantially.

[0148] Subsequently, BEKU [the dose of 1000 mJ/cm²] in whole surface UV Mitsuteru putting and 180-degree C oven for 1 hour after developing negatives by removing the exposure section using a 1 mass % monoethanolamine water solution. The thickness of the insulating layer which is a positive type photosensitivity (heat curing) resin layer by which was exposed completely and heat-curing processing was carried out was 1.3micro, the pencil degree of hardness was 6H, and the dielectric constant was 2.8 (1kHz). The size of a bottom of the configuration of the contact hole section was mortar-like [with a tilt angle good at 28 degrees] in 8 micrometerphi (development nature is good). Moreover, it was substantially transparent and colorless and light transmittance was 95% on the wavelength of 350nm. The sputter of ITO was performed from besides and the transparent conductive layer of 0.2-micrometer thickness was formed.

[0149] Besides carry out spreading desiccation of the photoresist, and the mask which has the pattern of a transparent electrode is exposed in piles. The ITO part which is not covered with the resist after development by acid etchant after etching The mixed solution of monoethanolamine and dimethyl sulfoxide (mass ratio 7:3) is used. When 80 degrees C was immersed for 10 minutes and the photoresist was exfoliated, the photoresist exfoliated, there is also no peeling of ITO in an insulating layer, and the damage on Siwa by swelling etc. was not accepted in it, either (exfoliation liquid resistance is good). Moreover, in this multilayer positive type photosensitivity (heat curing) resin layer imprint ingredient, although processing same after neglect for four days was performed at 50 degrees C, it was admitted that there was no change in engine performance, such as development nature, (stability with the passage of time is good).

[0150] Except changing the copolymer 1 in the coating liquid C7 of the [example 8] example 7 into a copolymer 4, the multilayer positive type photosensitivity (heat curing) resin layer imprint ingredient was created like the example 8, and processing and evaluation were performed similarly. Development nature, exfoliation liquid resistance, and stability with the passage of time were good like the example 7.

[0151] The copolymer 1 in the coating liquid C7 of the [example 10 of comparison] example 7 was changed into the copolymer (copolymerization mole ratio 28/72, mass average-molecular-weight ** 30,000) of a methacrylic acid / methacrylic-acid benzyl ester, and except newly adding the compound 10.0 mass section of the example 1 of comparison composition, the multilayer positive type photosensitivity (heat curing) resin layer imprint ingredient was created like the example 7, and it evaluated similarly. Although development nature was good, when exfoliating

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is process drawing for explaining the manufacture approach of the transparent conductive wiring version using the photosensitive (heat curing) resin constituent of this invention.

[Drawing 2] It is the sectional view of the photosensitive (heat curing) resin layer imprint ingredient of this invention.

[Drawing 3] It is the sectional view of the multilayer photosensitive (heat curing) resin layer imprint ingredient based on this invention.

[Description of Notations]

- A process Preparation of an ITO wiring substrate
- B process Formation of a photosensitive (heat curing) resin constituent layer
- C process Pattern exposure through a mask
- D process Development
- E process Postexposure and BEKU
- F process Formation by the spatter of the ITO film
- G process Etching-resist spreading desiccation, pattern exposure
- H process Etching-resist development
- I process Etching-resist exfoliation
- 11 Glass Substrate
- 12 Bottom ITO Pattern
- 13 Photosensitive (Heat Curing) Resin Layer
- 14 Photo Mask
- 15 On [ITO]
- 16 Etching Resist
- 21 Temporary Base Material
- 22 Photosensitive (Heat Curing) Resin Layer
- 23 Protection Film
- 31 Temporary Base Material
- 32 Alkali Fusibility Thermoplastics Layer
- 33 Interlayer
- 34 Photosensitive (Heat Curing) Resin Layer
- 35 Protection Film

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